# Ionization Energies and Thermal Fragmentation Patterns of Gaseous Cyclopoly-arsanes and -phosphanes $E_nR_n$ (E = As or P; R = Me, Bu$^t$, or $CF_3$; $n$ = 3—5): A Joint Temperature-variable Field Ionization Mass Spectrometric and Ultraviolet Photoelectron Spectroscopic Study†

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Ultraviolet photoelectron spectroscopic (u.p.s.) data for gaseous $As_4Bu^t_4$, $As_4(CF_3)_4$, and $As_5Me_5$ are presented and discussed with respect to the known ionization potentials of the parent cyclopoly-phosphanes. Pyrolytically induced fragmentation patterns of representative cyclopoly-phosphanes and -arsanes in the gas phase have been analysed by high-temperature field ionization mass spectrometry (f.i.m.s.) and u.p.s. Evidence for a thermally generated transient phosphinidene $P(CF_3)$ from $[P(CF_3)]_n$ ($n$ = 4 or 5) in the gaseous phase is provided by f.i.m.s., whereas products such as $P_2$ and $CF_2$ from secondary reactions are revealed by u.p.s. The u.p.s. upon thermal fragmentation of $Sb(CF_3)_3$ is also presented.

The synthesis of Group 15‡ ring systems has received considerable attention since the recognition of their structural relationship to carbocycles.[1] Unlike their carbon counterparts, Group 15 heavy atoms do not tend to form multiple bonds under normal experimental conditions.[2] This behaviour, known as the 'double bond rule,' has in recent years become a challenge to both experimentalists and theoreticians and has caused several structural revisions.[2b,c,3] Our interest in the gas-phase reactivity and electronic structures of inorganic ring systems in general originates from joint u.v. photoelectron spectroscopic (u.p.s.) and field ionization mass spectroscopic (f.i.m.s.) studies of their thermal fragmentation patterns, which gave evidence of new gaseous intermediates with hitherto unknown bonding properties.[4] The present study is directly related to the thermal [2 + 1]-retrocycloaddition reaction of $(Bu^tPNBu^t)_2$ studied by Niecke *et al.*;[5] the thermal fragmentation of this compound was chosen by us as a gas-phase model relation to test the combination of u.p.s. and m.s.[4a]

The present investigation is restricted to homonuclear ring systems with special emphasis on the photoelectron spectra of cyclopolyarsanes. A range of Group 15 heteronuclear systems such as $(Bu^tNPCl)_2$, $Me_3As_3S_3$, $Me_3P_3O_6$, $N_4P_4R_8$ *etc.*, will be reported elsewhere.[6]

## Results and Discussion

*U.v. Photoelectron Spectroscopy.*—The cyclopoly-arsanes and -phosphanes were selected in order to elucidate their electronic structures (thereby indirectly also their molecular structures) in terms of ionization potential (i.p.) patterns, and their unimolecular fragmentation behaviour upon pyrolysis in the gas phase as a function of ring size ($n$ = 3—5), the heavy atom (P or As), and/or the substituents (R = Me, $CF_3$, or Bu$^t$). Overlap with earlier u.p.s. studies on cyclopolyphosphanes and mixed derivatives[7-9] could not therefore be fully avoided; the respective literature spectra have been utilized here as references (dashed lines in the figures). The vertical i.p.s (band maxima) are summarized in the Table.

Figure 1(*a*) and (*b*) show the He I$\alpha$ photoelectron spectra of gaseous t-butyl and trifluoromethyl cyclotetra-arsanes correlated with those of the corresponding phosphanes [$P_4Bu^t_4$, *cf.* refs. 7, 8; $P_4(CF_3)_4$, *cf.* ref. 7]. For the latter, the spectra of the pyrolyzates, at the tube temperatures indicated, are also included. Comparing the spectra of the four unpyrolyzed precursors, it appears that all spectra may be roughly subdivided into three parts each, (*a*) the respective lowest-energy band groups unambiguously associated with ionizations from the lone-pair molecular orbitals (m.o.s), $n_E$, (*b*) the respective second, more or less resolved band systems assigned mainly to i.p.s from the $\sigma$ skeletal E–E and E–C bonding m.o.s, respectively, and (*c*) the broad featureless peaks found for the butyl derivatives between *ca.* 11 and 16 eV [Figure 1(*a*)], which appear rather insensitive to the P to As exchange and assigned accordingly to i.p.s from the $\sigma_{C-C}$ and C–H bonds. The same insensitivity is true for the respective and characteristic $n_F$ and $\sigma_{C-F}$ energy section, which we explain with respect to photoelectron data for $PH_2(CF_3)$[10] and the $E(CF_3)_3$ series[10] or of $HCF_3$ [*cf.* Figure 1(*b*)].[11] Bands ascribed to $\sigma_{E-E}$ and $\sigma_{E-R}$ energies, *i.e.* to m.o.s containing appreciable heavy-atom character, are more shifted [following directly the trends of the atomic $E_p$ valence-shell ionization potentials (v.s.i.p.s)], in any case more than the respective $n_E$ i.p.s in Figure 1, and are thus identified. This is fully consistent with the findings presented earlier for the i.p. trends of the $ER_3$ series.[10] As expected from the relative positions of the v.s.i.p.s of atomic As and P and as established for a range of representative phosphanes and arsanes, the respective cyclotetra-arsanes often possess slightly lower first i.p.s than their lighter counterparts (however, note the reversed i.p.$_1$ positions for $P_3Bu^t_3$ and $AsP_2Bu^t_3$[8] and $PMe_3$ and $AsMe_3$[10]). Since no interchange within the i.p. level ordering is expected upon replacing P by its heavier congeners, the assignments for both cyclotetra-arsanes are straightforward by reference to those of the phosphanes[7,8] and to qualitative considerations. It should be stressed that, due to the band shifts occurring upon the replacement of P by As, the photoelectron spectrum of $As_4Bu^t_4$ is far better resolved thus helping to clarify the discrepancies between the assignments presented earlier for $P_4R_4$.[7,8] To rationalize the underlying low-energy m.o. sequence for the Bu$^t$ derivatives [Figure 1(*a*)], qualitative m.o. models including transannular interactions assisted by calcula-

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† *Non-S.I. unit employed:* eV = $\approx 1.60 \times 10^{-19}$ J.

‡ Refers to the 18-Group format of the Periodic Table.

**Table.** Photoelectron band maxima (eV) for $E_nR_n$ ring systems[a]

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $P_4Bu^t_4$[b] | 7.36 | 7.85 | 9.33 | 9.91 | 10.1 (sh) | 11.5 | 12.9 | 14.7 | | | |
| $As_4Bu^t_4$ | 7.32 | 7.73 | 8.69 | 9.45 | 9.90 | 11.1 | 12.4 | 14.4 | | | |
| $P_4(CF_3)_4$[c] | 10.12 | 10.58 | 12.37 | 12.92 | *ca.* 13.66 (sh) | 15.36 | 15.96 (sh) | 17.05 | | | |
| $As_4(CF_3)_4$ | 9.73—10.06 | | 11.61 | 12.43 | 15.36 | 16.82 | He IIα: | *ca.* 20.1(2) | *ca.* 23.5(1) | | |
| $P_5Me_5$[d] | 7.58 | 7.93 | 8.69 | 9.01 | 9.76 | | | | | | |
| $As_5Me_5$ | 7.51 | 7.77 | 8.30 | 8.56 | 8.85 | 9.39 | 9.85 | 10.78 | 11.24 | 13.6 | 18.9 |

[a] sh = Shoulder; numbers in parentheses refer to He II band intensities. [b] See also refs. 7, 8. [c] See also ref. 7. [d] Taken from ref. 9.

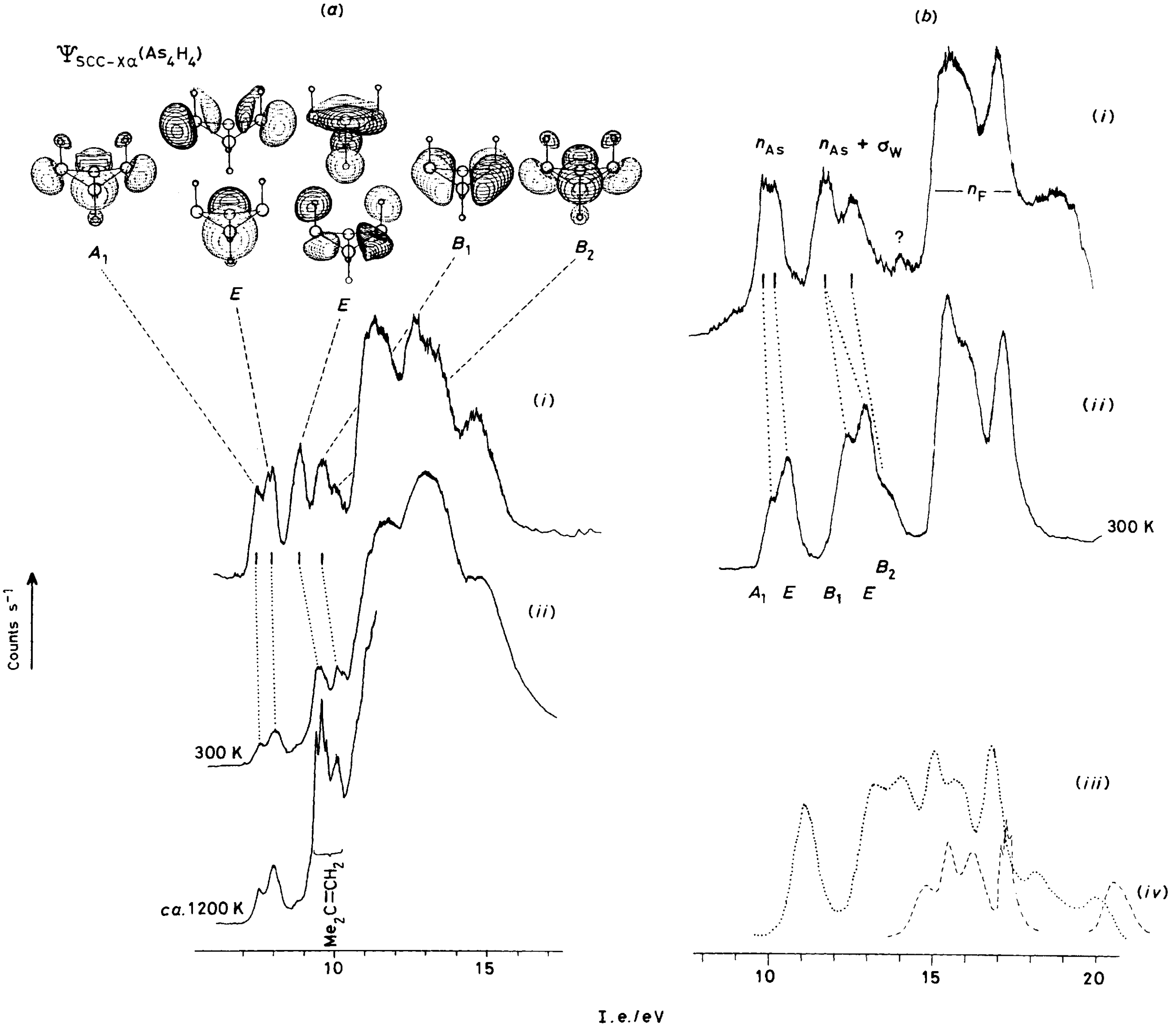

Figure 1. He Iα photoelectron spectra of (*a*) $As_4Bu^t_4$ (*i*) and $P_4Bu^t_4$ (*ii*) assigned qualitatively and according to ref. 8 and to SCC-Xα m.o. diagrams for the parent '$As_4H_4$'; $Me_2C{=}CH_2$ is eliminated upon thermolysis of $P_4Bu^t_4$ (*cf.* superposed spectra at the bottom); (*b*) $As_4(CF_3)_4$ (*i*) and $P_4(CF_3)_4$ (*ii*) correlated; literature spectra of $PH_2(CF_3)$[10] (*iii*) and $HCF_3$[11] (*iv*) are also shown

tions at various stages of sophistication, substituent effects, and band-intensity criteria have been employed without definitive answer.[7,8] Since SCC-Xα model calculations[12] for the prototype $As_4H_4$ failed to solve the problem, one has to rely on qualitative considerations: the third and fourth bands of $As_4Bu^t_4$ are the more shifted than those of $P_4Bu^t_4$ [Figure 1(*a*)], thus suggesting that m.o.s with predominant $\sigma_{As}$ character are involved instead of the typical $n_{As}$ m.o. ($B_2$) (however, note the strong mixing between $n_{As}$, 'Walsh,' and $\sigma_{As-R}$ m.o.s for symmetry and energy reasons). The sequences given in Figure 1(*a*) and (*b*) are in agreement with the intensity pattern of 1:2:2:(1 + 1) as already pointed out for the cyclophosphane in ref. 8. The m.o. illustrations in Figure 1(*a*) based on this qualitatively derived sequence refer to SCC-Xα m.o. plots for the

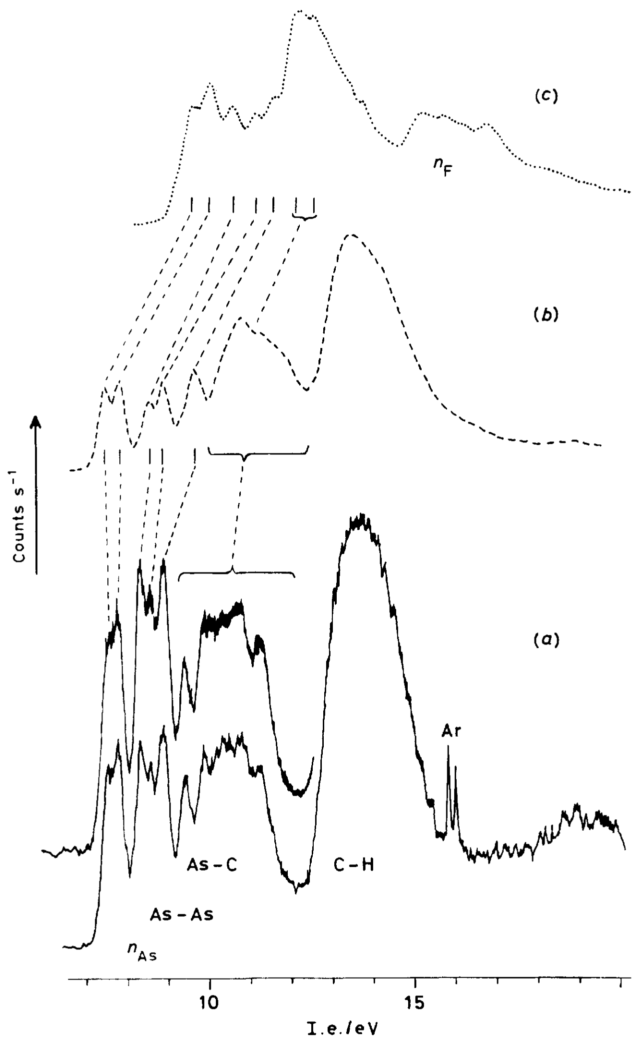

**Figure 2.** He I$\alpha$ photoelectron spectrum of (*a*) pentamethylcyclopenta-arsane correlated with literature spectra of (*b*) $P_5Me_5$[9] and (*c*) $P_5(CF_3)_5$[7]

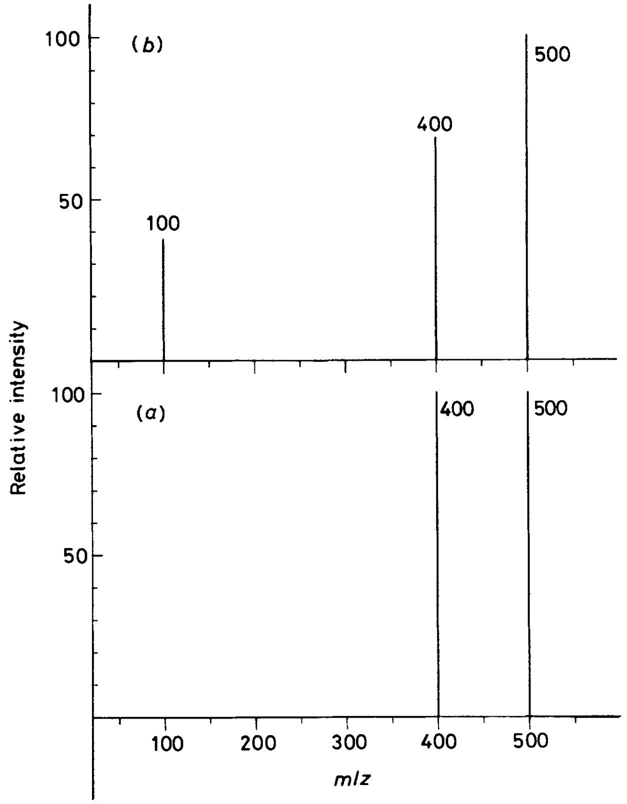

**Figure 3.** F.i.m.s.: (*a*) $[P(CF_3)]_n$ ($n$ = 4 or 5) and (*b*) following pyrolysis at 1 404 K, the samples being introduced by injections of diethyl ether solutions

occupied frontier m.o.s of the $As_4H_4$ model. With respect to the relative photoelectron i.p.s of the pairs $AsH_2(CF_3)$ and $AsH_2Me$ or $As(CF_3)_3$ and $AsMe_3$[10] no i.p. reversal is expected on going from $E_4R_4$ (R = alkyl) to $E_4(CF_3)_4$ [*cf.* $P_5(CF_3)_5$ and $E_5Me_5$, Figure 2], thus leading to analogous assignments [Figure 1(*b*); unavoidable traces of $As_5(CF_3)_5$ impurities are responsible for the relatively high background of the spectrum of $As_4(CF_3)_4$].

Group 15 $E_5R_5$ ring systems are subject to pseudorotation[13] and their complex photoelectron spectra should, if thoroughly analyzed, be treated accordingly.[9] Although the overall similarity between the photoelectron spectra of $As_5Me_5$ and $P_5Me_5$ (Figure 2) is retained, at least six, more or less superposed peaks within the low-energy section (*cf.* Table) can be identified. Whether this is an indication for distinct gaseous conformers as are typical for $R_2E$–$ER_2$ (E = P or As) molecules (*cf.* ref. 7 and refs. therein) is not fully conclusive since appreciable amounts of $As_3Me_3$ could be identified by f.i.m.s. in the $As_5Me_5$ samples which had not been recognized earlier by n.m.r. spectroscopy[13] (the presence of impurities from $As_nMe_n$ with $n \neq 3$ or 5 could be excluded in this way). It should be stressed that the equilibrium $\frac{3}{5}P_5Me_5 \rightleftharpoons P_3Me_3$ has been observed by Baudler *et al.*,[14] however the authors did not succeed in trapping the three-membered ring species. Keeping in mind that strong mixing of $n_{As}$, As–As, and As–C m.o.s is predetermined, the approximate assignment is as depicted in Figure 2 following the rough i.p. sequence $|n_{As} <$ As–As $<$ As–C$|$. For a more precise analysis ref. 9 should be consulted. Since the band intensities seem to be insufficiently reproduced for $P_5(CF_3)_5$[7] further consideration is unwarranted.

*Thermal Fragmentations.*—The pyrolytically induced reactions of $P_4Bu^t_4$ and $[P(CF_3)]_n$ ($n$ = 4 or 5) were studied by f.i.m.s. as well as u.p.s. Pyrolysis of $P_4Bu^t_4$ in the temperature range 800—1 050 K resulted exclusively in formation of two species with molecular weights 124 and 56, respectively, which were assigned to $P_4$ and 2-methylpropene, respectively. Formally, the reaction can be rationalized as cleavage of the P–C bonds according to equation (1). Since the $Bu^t$ radical is

$$P_4Bu^t_4 \longrightarrow 4Bu^{t\bullet} + P_4 \longrightarrow Me_2C{=}CH_2 \qquad (1)$$

too short-lived to be trapped under the prevailing experimental arrangement (*cf.* Experimental section) only its product of rearrangement, namely $Me_2C{=}CH_2$, appears in the photoelectron spectrum [Figure 1(*a*)] (*cf.* ref. 15). The remaining $P_n$ species escape detection because of serious band superposition due to at least three different species being present simultaneously.

In the case of $[P(CF_3)]_n$ ($n$ = 4 or 5) a completely different course of reaction was observed. In Figure 3 f.i.m.s. spectra of these systems and the reaction mixture following gas-phase Curie-point pyrolysis (*cf.* Experimental section) of the latter are shown. Unambiguously, pyrolysis afforded formation of a new species with molecular weight 100, which for obvious reasons could be assigned to $P(CF_3)$ [equation (2)]. The generation of

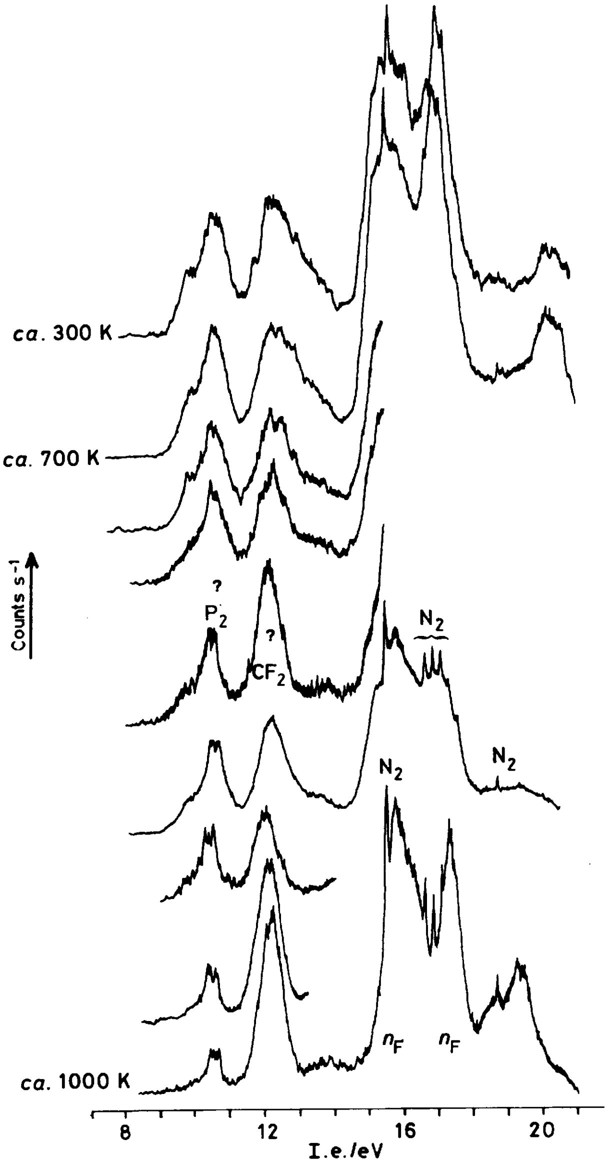

**Figure 4.** Photoelectron spectrum of $P_4(CF_3)_4$ at ambient and high temperatures using a gold-coated alumina inlet tube (calibrant gas: $N_2$)

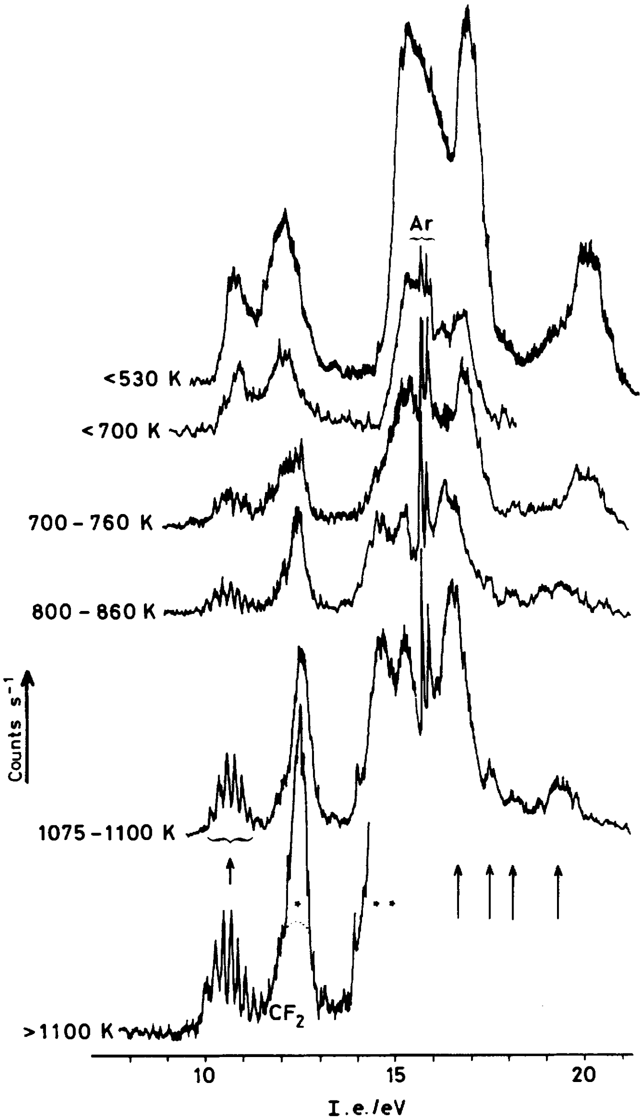

**Figure 5.** Photoelectron spectrum of $Sb(CF_3)_3$ at ambient and high temperatures using a $Al_2O_3$ heated inlet tube. Bands marked by arrows refer to $C_2F_4$, those marked by asterisks are due to a yet unidentified species

$$[\mathrm{P(CF_3)}]_n \longrightarrow n\,\mathrm{P(CF_3)} \qquad (n = 4 \text{ or } 5) \qquad (2)$$

free phosphinidenes, PR, from respective cyclopolyphosphanes by thermal degradation has long been known.[16a] Their fixation through complexation[16b,c] is of current interest since their relationship to isosteric carbyne moieties RC: has been recognized. The orbital-energy patterns of a range of phosphinidenes including those void of possibilities for π delocalization have recently been calculated by Trinquier and Bertrand.[16b]

Pyrolyses of the corresponding arsanes $As_4R_4$ apparently caused elimation of $R^{\bullet}$. In the case of $R = \mathrm{Bu^t}$, 2-methylpropene was detected. However, we were unable to observe any As-containing products in the pyrolyzate. Likewise, in the case of $[\mathrm{As(CF_3)}]_n$ ($n = 4$ or 5), which appeared surprisingly stable, minor amounts of $^{\bullet}CF_3$ were the only detectable pyrolysis product. In this connection it can be noted that pyrolysis of the five-membered $As_5Me_5$ ring gave rise to formation of two products with molecular weights 120 and 210, assigned to $AsMe_3$ and $Me_2As$–$AsMe_2$, respectively.

Finally, in the pyrolysis of $\mathrm{P_3Bu^t_3}$, according to f.i.m.s., the two major products were $Me_2C{=}CH_2$ and a compound with molecular weight 90, tentatively assigned to $\mathrm{PH_2Bu^t}$. Minor amounts of $P_4$ and '$\mathrm{(Bu^tP)_3}$-isobutene' could be observed.

When the pyrolytic decomposition of $[\mathrm{P(CF_3)_4}]_n$ ($n = 4$ or 5) is monitored by u.p.s. (Figure 4), band-intensity changes develop at *ca.* 700 K with concomitant $n_F$-band shifts to somewhat higher energies. On increasing the temperature of the pyrolysis zone ($Al_2O_3$ ceramics, gold-coated), there is a continuous decrease of the bands of $P_4(CF_3)_4$ leaving finally at least two well separated low-energy bands at 10.6 and 12.6 eV and at least one new $n_F$ band set. Among the various possible degradation products [*e.g.* '$P(CF_3)$', $P_4$, $P_2$, $CF_2$, $^{\bullet}CF_3$, or $C_2F_4$] there are two species that could together fit the high-temperature photoelectron band pattern (Figure 4), *i.e.* $CF_2$[17] and $P_2$.[18] However, although the resolution was satisfactory (*ca.* 20 meV), no vibrational fine structure could be detected in the second band at 12.6 eV, which could otherwise well suit the first photoelectron band of $CF_2$.[17] Although these two low-

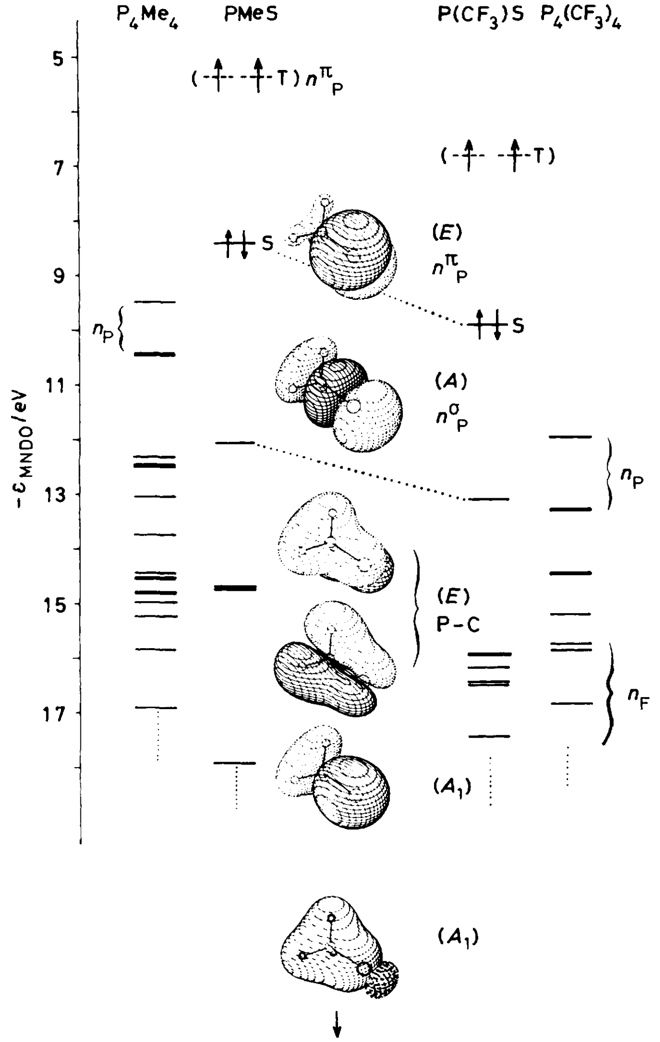

Figure 6. MNDO eigenvalues for $P_4Me_4$, PMe, $P(CF_3)$, and $P_4(CF_3)_4$ including eigenvector plots for singlet PMe (S = singlet state, T = triplet state). The irreducible representations refer to the $C_{3v}$ symmetry of the triplet species

energy bands would also fit the pattern of the expected $P(CF_3)$ monomer (however, not that of isomeric $CF_2{=}PF$), which presumably should possess a singlet ground state in correspondence with PX (X = halogen),[16b] we tried to limit the speculations in two ways. (*i*) We also measured the photoelectron spectrum of the stibane $Sb(CF_3)_3$ under analogous variable-temperature conditions to discern contributions from free $CF_3$ radicals or their rearrangement products ($CF_2$, $CF_4$, $C_2F_4$, and $C_2F_6$). The antimony species is expected to lose $CF_3$ radicals readily at temperatures below 300 °C. The results are depicted in Figure 5. (*ii*) We performed model calculations within the frame of the MNDO approximation[19] for the $P(CF_3)$ monomer (taking into account both singlet and triplet ground states) as well as for the tetramer in order to get an indication of the position of the frontier levels of the occupied orbital set of $P(CF_3)$ in relation to the energies of the tetramer. Furthermore, to elucidate the shapes of the m.o. types involved we plotted the MNDO eigenvectors[20] (occupied levels) of the simpler parent PMe which is expected to possess σ-type m.o.s analogous to the skeletal m.o.s of $CF_3$ (*cf.* ref. 10). For consistency, the MNDO energy levels of $P_4Me_4$ have also been included. The results are summarized in Figure 6. As is evident from this figure, phosphinidenes exhibit two low-energy m.o.s, the highest occupied molecular orbital (h.o.m.o.) being of π type ($n_P{}^{\pi}$) for both the singlet (S) and triplet (T) ground states and the second highest m.o. being P–C bonding with a large $n_P{}^{\sigma}$ contribution. Upon ionization at least the h.o.m.o. should give rise to a photoelectron band exhibiting a steep low-energy Franck-Condon envelope. Provided the model calculations presented here are reliable enough, one should search for the two exposed $n_P$ (π and σ) bands of the presumed $P(CF_3)$ in the neighbourhood of the first band complex of $P_4(CF_3)_4$, which was associated with ionizations from $n_P$-based m.o.s or even at lower energies. Since our spectra are scanned from the $He^+$ line (4.99 eV) we may conclude that no other bands except the ones mentioned above could be detected within the 5—13 eV region.

The thermolysis of $Sb(CF_3)_3$ obviously yielded at least three new gaseous species (Figure 5). Two are probably secondary products and can unambiguously be assigned to $CF_2$ and $C_2F_4$.[17] However, as indicated, the first band of $CF_2$ is obscured by a second component. Since free $CF_3$ is known to have a first i.p. in the region 9.25—10.10 eV,[21] where $C_2F_4$ shows a long vibrational progression ($i.p._1$) (Figure 5), the presence of $CF_3$ radicals can thus be excluded. Whether the third species (the respective bands are designated by asterisks in Figure 5) is a fluorine-substituted stibane [*e.g.* $SbF_2(CF_3)$] or even $Sb(CF_3)$ cannot be disclosed at this stage of the investigation.

Returning to the photoelectron spectra of the pyrolyzate of gaseous $P_4(CF_3)_4$ (Figure 4), we conclude that the spectroscopic identification of $P(CF_3)$ fails upon accidental coincidence of its two low-energy bands with those of the observed decomposition products $P_2$ and $CF_2$. So far, the spectroscopic results neither exclude nor confirm the possibility that free transient $P(CF_3)$ has been generated as the primary product of unimolecular decomposition. Investigations using shorter paths (< 5 cm) between the pyrolysis zone and ionization chamber are in progress.

## Experimental

The He I and He II photoelectron spectra of the arsanes were recorded on a 0078 Helectros spectrometer with a pyrolysis device (H. J. Lempka, Beaconsfield) and were calibrated using the argon doublet and the $He^+$ lines. The He I spectra of the phosphanes were recorded at different temperatures using an UPG 200 spectrometer from Leybold-Heraeus, Cologne. Details of its pyrolysis equipment have been described elsewhere.[4a] The temperatures quoted were measured at the walls of the molybdenum (UPG 200) or the gold-coated alumina inlet tube (Helectros). The i.p.s are quoted to an estimated accuracy of ±0.10 eV for the phosphanes and ±0.05 eV for the arsanes.

Mass spectrometric investigations were carried out using a Varian Mat CH 5D double-focusing mass spectrometer equipped with a combined electron impact (e.i.)–field ionization (f.i.)–field desorption (f.d.) ion source. The f.i. spectra were obtained using a 10-μm tungsten wire, activated in benzonitrile vapour as emitter.

The pyrolyses were carried out by application of the low-pressure Curie-point pyrolysis technique, which has been previously described in detail,[22] where the pyrolysis products are introduced directly into the ion source of the mass spectrometer. In all cases gold-plated Curie-point pyrolysis filaments were used in order to suppress possible surface-promoted reactions.[23] Pyrolyses were carried out in the temperature range 783—1 404 K (filament temperature, *cf.* ref. 24).

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